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SYNTHESIS, PHYSIOCHEMICAL PROPERTIES AND BIOLOGICAL ACTIVITY OF N,O,O DONOR SCHIFF BASE AND ITS CU(II), NI(II), CD(II), MN(II) AND CO(II) COMPLEXES

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Abstract. A Schiff base ligand (H₂L), {2-((2-hydroxybenzylidene)amino)benzoic acid}(C₁₄H₁₁NO₃) containing nitrogen-oxygen donor atom was prepared by the condensation of salicylaldehyde and anthranilic acid and coordinated with Cu(II), Ni(II), Cd(II), Mn(II) and Co(II) ions. The Schiff base and its metal complexes were characterized by elemental analysis, FT-IR, ESI-MS, electronic absorption spectroscopy and some of their physicochemical properties were determined. The overall reaction was monitored by TLC analysis. The analytical and theoretical data showed that the metal ligand stoichiometry in the complexes was 1:1. Molar conductance study have shown that all the complexes were non electrolytic in nature. FT-IR studies suggested that Schiff base acts as deprotonated tridentate ligand and metal ions are attached with the ligand- by azomethine nitrogen, oxygen atom of deprotonated hydroxyl group and deprotonated oxygen of the carboxyl group of ligand respectively. Thermal analysis (TGA and DTG) data suggested that, a small weight loss occurred in the range of 40°C – 80°C from the complex which is assigned to the loss of lattice water and maximum weight loss in the range of 280- 450 °C is attributable to the loss of coordinated water present in all complexes. These data also showed that most of the complexes were thermally stable up to 200^{0} C. All the complexes showed good antimicrobial activity compared to ligand and commercial standard.

Keywords: Schiff base, metal complexes, FTIR, UV-visible, thermal analysis, biological activity.

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1. Introduction

Nitrogen-oxygen donor Schiff base ligands have attracted great interest of researchers, because they have potentially donor atoms which are sterically available for metal chelation. Researchers in this area have synthesized new nitrogen-oxygen donor ligands by the condensation of aldehydes and amines (Liu & Hamon, 2019; Zhang *et al.*, 2018; Hossain *et al.*, 2016) The number of synthesized ligands continues to increase because of the intriguing observation that different ligands show different biological properties, even though they may only slightly differ in their molecular structure (Seco *et al.*, 2000; Soliman *et al.*, 1989; Raman *et al.*, 2001; Islam *et al.*, 2020; Mohapatra *et al.*, 2019). Metals have played a significant role in biological systems over the years. Many are important to our diets in varying quantities, although people have only recently realized their significance. Incorporating metal ions into a biological system may be carried out for therapeutic or diagnostic purposes, although these purposes overlap in many cases. Metals not only provide path for synthesis, but they also introduce functionalities that enhance drugs action. Antibiotic resistance has been

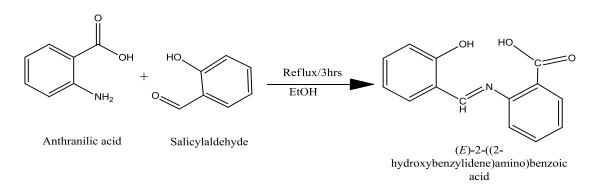
growing at an alarming rate and consequently, the activity of antibiotics against Gramnegative and Gram-positive bacteria has dropped dramatically day by day. In this sense there is a strong need to synthesis new substances that not only have good spectrum of activity, but having new mechanisms of action. When metals are coordinated to ligand specially Schiff base, they show more biological activity such as antibacterial, antiviral, anti-cancer, antitumor, anti-HIV, anti-oxidant etc. than their corresponding ligands. In this paper, we mainly focus on synthesis, characterization and antimicrobial activity study of some metal complexes containing Schiff base.

2. Experimental Data

All chemicals and solvents used were of analytical grade. All metal (II) salts were used as nitrate, chloride and sulphate. The solvents such as ethanol, methanol, chloroform, diethyl ether, petroleum ether and acetonitrile were purified by distillation procedure. The melting point or the decomposition temperature of the prepared ligand and metal complexes were observed in an electro thermal melting point apparatus model No. AZ6512. Infrared spectra were recorded on a FTIR-8400, SHIMADZU, Japan using a KBr disc, in Central Science Lab of Rajshahi University. Thermo gravimetric analysis (TGA) was performed on Perkin Elmer Simultaneous Thermal Analyzer, STA-8000. The ¹H-NMR spectra were taken from BCSIR, Dhaka, Bangladesh. The electronic spectrum of the complex in solution phase $(5 \times 10^{-4} \text{ M})$ was recorded on a Shimadzu Double Beam spectrophotometer model UV-1200 and UV-1650PC. ESI-MS spectra were done with an Agilent Technologies MSD SL Trap mass spectrometer with ESI source coupled with an 1100 Series HPLC system. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used to measure the magnetic moment of the solid complexes following the Gouy method. The electrical conductance measurements were made at room temperature in freshly prepared aqueous and DMSO solution $(10^{-3}M)$ using a WPACM35 conductivity meter and a dip-cell with a platinum electrode. The purity of the ligand and metal complexes were tested by Thin Layer Chromatography (TLC).

Synthesis of Schiff base Ligand (H₂L) C₁₄H₁₁NO₃

Anthranilic acid (3.43g, 25mmol) was dissolved in absolute ethanol (15 mL) and stirred for 30 minutes. Then ethanolic (15 mL) solution of salicylaldehyde (2.62 mL, 25 mmol) was added slowly to a constant stirring solution of anthranilic acid and the mixture was refluxed for 3 hours. On cooling, a solid orange color product was formed which was filtered, washed with ethanol, diethyl ether and dried in vacuum over anhydrous CaCl₂. The reaction was monitored by TLC using petroleum ether, ethyl acetate and methanol solvents. The product was found to be soluble in methanol, chloroform, DMF and DMSO and insoluble in acetone, diethyl ether and Petroleum ether. Yield: 90 %, m.p: 185-186⁰C. ¹H NMR spectrum, δ , ppm: 15.35 s (-C-OH), 11.2 s (-CO-OH), 8.85s (-CH=N-), *Anal.* Calc. For C₁₄H₁₁NO₃: C=69.70, H=4.56, N=5.80, O=19.91%, Found: C=69.25, H=4.30, N=5.50, O=19.21%.

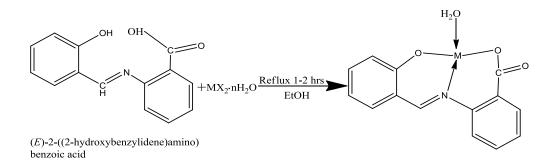


Scheme 1. Synthesis pathway of the Schiff base ligand, $C_{14}H_{11}NO_3$

Preparation of Schiff Base Ligand Metal Complexes

The complexes were prepared in 1:1 molar ratio (metal: ligand). During complexation reaction a warm 20 mL ethanolic solution (0.2413g, 1mmol) of prepared Schiff base ligand ($C_{14}H_{14}NO_3$) was taken in a two necked round bottom flask and kept on magnetic stirring. 10 mL hot ethanolic solution of copper(II) nitrate tri-hydrate (0.241g,1 mmol) / Manganese(II) sulphate mono-hydrate (0.169g, 1 mmol)/ Nickel(II) nitrate hexa-hydrate (0.291g, 1 mmol)/Cadmium(ll) nitrate tetra-hydrate (0.308g,1mmol)/Cobalt(II) chloride hexa-hydrate (0.237g,1mmol) salt was added drop wise and stirred with heating for 4-5 hours. On cooling, precipitates were formed which were filtered, washed with ethanol, acetone, and diethyl ether and dried in vacuum desiccators over anhydrous CaCl₂. The purity of each complexes was checked by TLC using petroleum ether, ethyl acetate and methanol solvents. The complexes were soluble in DMSO and DMF. The synthesis pathway of complexes is shown in (Scheme 2).

[Cu (L)]:- Color: Pest; m.p: 268-270°C; yield: 75%
[Ni (L)]:- Color: Off white; m.p: >300°C; yield: 70%
[Cd (L)]:- Color: Gray; m.p: >300°C; yield: 75%
[Mn (L)]:- Color: Light yellow; m.p: >300°C; yield: 85%
[Co (L)]:- Color: Off white; m.p: >300°C; yield: 63%



Scheme 2. Synthesis pathway of Schiff base metal complexes [MC₁₄H₁₁NO₄], where M= Cu(II), Mn(II), Ni(II), Co(II), Cd(II)

3. Results and Discussions

FT-IR spectrum of Schiff Base ligand C₁₄H₁₁NO₃ (H₂L) and metal complexes

The IR characteristic bands were given in Table 1. The spectrum of the ligand showed a strong absorption band at 1617 cm⁻¹ due to the azomethine v(C=N) stretching frequency of the free ligand indicating that the condensation has taken place between the CHO moiety of salicylaldehyde and $-NH_2$ moiety of anthranilic acid. The band observed at 3435 cm⁻¹ was assigned to the v(O-H) of hydroxyl group (Soliman *et al.*, 1989; Jezowska-Trzebiatowska *et al.*, 1988). A band at 1562cm⁻¹ is assigned to v(C=O) stretching frequency in the spectrum of free Schiff base (Soliman *et al.*, 1989; Jezowska *et al.*, 1981). The strong band at 1385 cm⁻¹ for v(C-O) indicated that C-O bond was present in the Schiff base ligand (Seco *et al.*, 2000; Soliman *et al.*, 1989; Raman *et al.*, 2001; Islam *et al.*, 2020; Mohapatra *et al.*, 2019; Jezowska-Trzebiatowska *et al.*, 1988; Jain *et al.*, 1981).

The FT-IR spectrum of the free ligand is compared with the spectra of the complexes. The main IR bands and their assignments are listed in Table 1. The IR band assignments of all metal complexes exhibit broad bands in the range of 3305 to 3436 cm⁻¹ indicating the presence of coordinated water molecules (Soliman et al., 1989; Lindoy et al., 1977). A band at 1617 cm⁻¹ in free Schiff base is due to v(C=N) stretching vibration. The shifting of this stretching to lower frequency (1614-1606 cm^{-1}) in the metal complexes when compared to free ligand, suggest the coordination of the ligand group (Soliman et al., 1989; with metal ion through nitrogen atom of azomethine Jezowska-Trzebiatowska et al., 1988; Singh & Singh, 2014). It is expected that coordination of nitrogen to the metal atom would reduce the electron density in the azomethine link and thus lower the -HC=N absorption. A band at 1562 cm⁻¹ is assigned to v(C=O) stretching frequency in the spectrum of free Schiff base which is also shifted to lower frequency ranging from 1554-1530 cm⁻¹ in all the metal complexes. This indicates the involvement of oxygen atom of hydroxy group of COOH group in bonding with metal ions (Soliman et al., 1989; Jezowska-Trzebiatowska et al., 1988; Konstantinovic et al., 2003). The v(C-O) (phenolic) stretching frequency of ligand is seen at 1385 cm⁻¹ which gets shifted to a frequency region in the complexes in the range of 1384-1409 cm⁻¹, and this is indicative of bonding through phenolic oxygen (Soliman et al., 1989; Jain et al 1981; Golcu et al., 2005). New bands, which are not present in the spectrum of ligand but appeared in the spectra of complexes in the range of 601-602 cm^{-1} , corresponding to v(M-O) and 313-419 cm⁻¹ to v(M-N) vibrations respectively. The appearance of v(M-N) and v(M-O) vibrations support the involvement of N and O atoms in complexation with metal ions under investigation (Soliman et al., 1989; Golcu et al., 2005). Therefore, the FT-IR spectral data indicate that the coordination sites of the metal ions are -C=N, -C-O and Ar-O (Seco et al., 2000; Jain et al., 1981; Lindoy et al., 1977; Alghool et al., 2003).

	FT-IR/cm ⁻¹							
Ligand / Metal Complexes	<i>v</i> (О-Н)	ν(C=N)	v(C-O)	v(C=O)	v(M-O)	v(M-N)		
Ligand (H ₂ L) C ₁₄ H ₁₁ NO ₃	3435	1617	1385	1562	-	-		
[Cu (L)] [CuC ₁₄ H ₁₁ NO ₄].H ₂ O	3436	1606	1384	1554	602	328		
[Ni (L)] [NiC ₁₄ H ₁₁ NO ₄]	3436	1614	1384	1541	602	313		
[Cd(L)] [CdC ₁₄ H ₁₁ NO ₄]	3435	1611	1384	1530	602	404		
[Mn(L)] [MnC ₁₄ H ₁₁ NO ₄].H ₂ O	3305	1614	1409	1543	602	412		
[Co(L)] [CoC ₁₄ H ₁₁ NO ₄].H ₂ O	3308	1614	1408	1538	602	419		

Table 1. Important IR spectral bands of the ligand and metal complexes

Table 2. Molar conductance, magnetic moments and electronic spectral data of the complexes

Compound	Observed conductivity (ohm ⁻¹ cm ² mol ⁻¹)	μ _{eff} Β.Μ	λ _{max} nm	Wave number /cm ⁻¹	Assignment
Ligand (H ₂ L) C ₁₄ H ₁₁ NO ₃		_	277 339	37735 29850	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[Cu (L)] [CuC ₁₄ H ₁₁ NO ₄].H ₂ O	2	1.97	260 340 405	38461 29411 24691	$ \begin{array}{c} \pi \rightarrow \pi^* \\ n \rightarrow \pi^* \\ \text{C.T} (M \rightarrow L) \end{array} $
[Ni (L)] [NiC ₁₄ H ₁₁ NO ₄]	5	1.14	255 365 480	39215 27397 20833	$\begin{array}{c} \pi \rightarrow \pi^{*} \\ \text{C.T (M \rightarrow L)} \\ 3A_{2g}(F) \rightarrow 3T_{1g}(F) \end{array}$
[Cd(L)] $[CdC_{14}H_{11}NO_{4}]$	3	0.86	260 338	38461 29585	$\begin{array}{c} \pi \rightarrow \pi^* \\ \text{C.T} (M \rightarrow L) \end{array}$
[Mn(L)] [MnC ₁₄ H ₁₁ NO ₄].H ₂ O	6	2.17	260 330	38461 30303	$\begin{array}{c} \pi \rightarrow \pi^* \\ \text{C.T} (\text{M} \rightarrow \text{L}) \end{array}$
[Co(L)] [CoC ₁₄ H ₁₁ NO ₄].H ₂ O	8	1.78	258 325	38759 30759	$\begin{array}{c} \pi \rightarrow \pi^* \\ \text{C.T} (\text{M} \rightarrow \text{L}) \end{array}$

Complexes	Steps	Temperature Range/ °C	TG mass loss% calc./found	DTG Peak /°C	Assignments
$[\mathbf{C}_{\mathbf{r}}(\mathbf{I})]$	1^{st}	35-120	5.30/5.20	55	H ₂ O
[Cu(L)]	2^{nd}	270-400	75.80/71.50	280	$C_{14}H_9NO_3\text{+}H_2O$
$[CuC_{14}H_{11}NO_4].H_2O$	3 rd	>450	23.50/26.80		Cu/CuO
[Ni (L)]	1 st	330-450	81.32/76.00	320	$C_{14}H_9NO_3+H_2O$
$[NiC_{14}H_{11}NO_4]$	2^{nd}	>450	23.41/22.50		Ni/NiO
[Mn(L)] [MnC ₁₄ H ₁₁ NO ₄].H ₂ O	1 st	35-90	5.47/4.50	50	H ₂ O
	2^{nd}	320-425	77.87/69.00	330	$C_{14}H_9NO_3\text{+}H_2O$
	3 rd	>430	22.00/28.00		Mn/MnO
[Co(L)] [CoC ₁₄ H ₁₁ NO ₄].H ₂ O	1 st	30-95	5.39/4.80	45	H ₂ O
	2 nd	330-450	76.94/72.10	340	$C_{14}H_9NO_3\text{+}H_2O$
	3 rd	>450	23.00/27.50		Co/CoO

 Table 3. Thermal data of metal complexes

ESI-mass Spectra

The ESI-Mass spectra of the ligand and complexes are presented in Fig.1. The obtained m/z values are similar to the formula weight which further supports the proposed structure of the synthesized compounds.

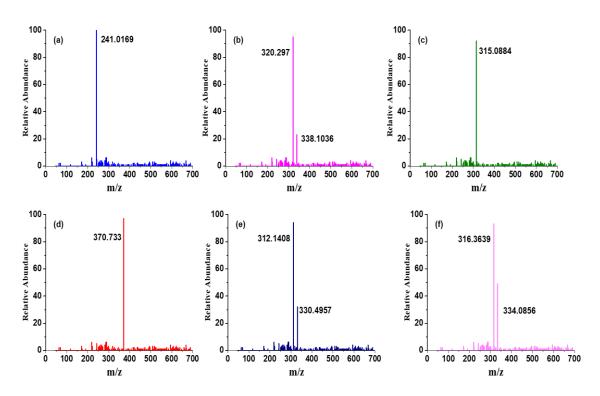


Figure 1. ESI-Mass spectra of the (a) L, (b) CuL, (c) NiL, (d) CdL, (e) MnL and (f) CoL

Compounds	Molecular Ion Peak (m/z)
Ligand (H ₂ L)	H_2L^+ (241.0169)
$C_{14}H_{11}NO_3$	
[Cu (L)]	$[Cu(L)(H_2O]^+ (320.297)$
[CuC ₁₄ H ₁₁ NO ₄].H ₂ O	
[Ni (L)]	$[Ni(L)(H_2O]^+ (315.0884)$
$[NiC_{14}H_{11}NO_4]$	
[Cd(L)]	$[Cd(L)(H_2O]^+ (370.733)$
$[CdC_{14}H_{11}NO_4]$	
[Mn(L)]	$[Ni(L)(H_2O]^+ (312.1408)$
$[MnC_{14}H_{11}NO_4].H_2O$	
[Co(L)]	$[Co(L)(H_2O]^+ (316.3639)$
$[CoC_{14}H_{11}NO_4].H_2O$	

Table 4. ESI-MS peak Assignments

Molar conductance, magnetic moments and electronic spectra

a. Electronic Spectrum of the Ligand (C₁₄H₁₁NO₃)

The UV-vis absorption spectrum of the ligand was recorded after dissolving into DMSO solvent at room temperature (Soliman *et al.*,1989; Jezowska-Trzebiatowska *et al.*, 1988) in the UV-visible range of 200-800 nm. The electronic spectrum of the ligand exhibits high intense absorption peaks at 277 nm and 339 nm which have been assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively (Soliman *et al.*, 1989; Islam *et al.*, 2020; Hossain *et al.*, 2017).

b. Electronic spectra of metal complexes

The UV-vis absorption spectra of the ligand and all complexes were recorded after dissolving into DMSO solvent at room temperature, in -UV-visible range of 200-800 nm. The UV-vis spectra of the Cu(II) complex showed three strong absorption bands in the UV-vis region of 200-800 nm, at 260, 340 and 405 nm. The peak at 260 nm is assigned to $\pi \rightarrow \pi^*$ and the peak at 340 nm is attributed to $n \rightarrow \pi^*$ transition due to lone pair of electrons of an azomethine nitrogen and an anti-bonding p orbital Sandras. (Konstantinovic et al., 2003; Golcu et al 2005; Hossain et al., 2018; Dalia et al., 2018). The presence of an absorption band at 405nm in the case of the complex assigned as a ligand-to-metal charge transfer (LMCT). The electronic spectra of Ni(II) complex showed three bands at 255, 365 and 480 nm. The peak at 255 nm is assigned to $\pi \rightarrow \pi^*$ and the peak at 365 nm is attributed to $n \rightarrow \pi^*$ transition due to lone pair of electrons of an azomethine nitrogen and an anti-bonding p orbital (Afsan et al., 2018; Dalia et al., 2018). The presence of an absorption band at 480 nm in the case of this complex corresponding to the transition $3A_{2g}(F) \rightarrow 3T_{1g}(F)$ of metal ion (Jezowska-Trzebiatowska et al., 1988; Afsan et al., 2018; Dalia et al., 2018; Hossain et al., 2018). UV-vis spectra of Cd(II),Mn(II)and Co(II) complexes showed two bands. Electronic spectra of Cd(II), Mn(II) and Co(II) complexes showed peak at 260, 260 and 258nm respectively. These

peaks are assigned to $\pi \rightarrow \pi^*$ transition for intraligand transition. Another band observed for these complexes at 338,330 and 325 nm respectively, which are attributed to the ligand-to-metal charge transfer (LMCT). From the above absorption band explanation of the ligand and complexes, we observed that these bands were shifted in the spectra of the corresponding metal complexes with some changes in the frequencies and intensities than ligand, which indicated the coordination of the ligand to the metal ions and the participation of the nitrogen atom of the azomethine group. The electronic spectra coupled with magnetic moment data (Table 2) suggested tetrahedral geometry for Cu(II), Cd(II), Mn(II), Co(II) Fig-(2-5) and square planar geometry for Ni(II) (Fig. 6) metal complexes.

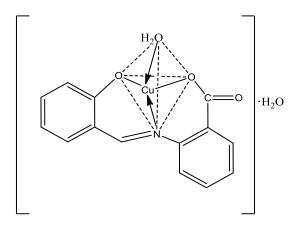


Figure 2. Proposed Structure of [CuC₁₄H₁₁NO₄].H₂O

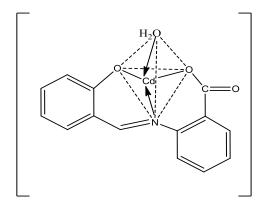


Figure 3. Proposed Structure of [CdC₁₄H₁₁NO₄]

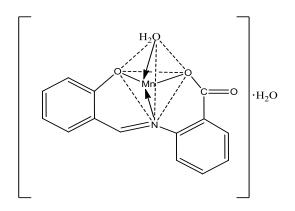


Figure 4. Proposed Structure of [MnC₁₄H₁₁NO₄].H₂O

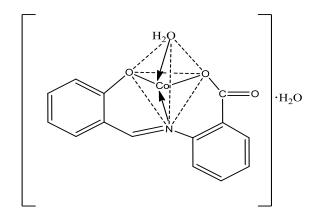


Figure 5. Proposed Structure of $[CoC_{14}H_{11}NO_4]$.H₂O

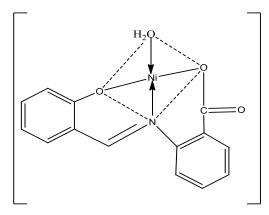


Figure 6. Proposed Structure of $[NiC_{14}H_{11}NO_4]$

Thermogravimetric analysis of metal complexes

The thermal analysis of solid Cu(II), Ni(II), Mn(II) and Co(II) metal complexes were carried out under nitrogen atmosphere and heating rate was suitably controlled at 30° C min⁻¹ and the weight loss was measured from the ambient temperature up to 800° C.The data from TGA and DTG clearly indicated that the decomposition of the

complexes proceed in two or three steps. There were some minor steps and asymmetry of TGA/DTG curves also observed. The weight losses for each complex was calculated within the corresponding temperature ranges. The different thermodynamic parameters are listed in Table 3. The TGA and DTG curve of Cu(II), Mn(II) and Co(II) complexes indicated that they decomposed into three main steps (Fig. 7,9-10) and Ni(II) complex (Fig. 8) was decomposed into two steps. In the first step of decomposition of Cu(II), Mn(II) and Co(II) complexes, at temperature range 30-120°C (calculated 5.30-5.47% and experimental 4.50-5.20%), are assigned to the loss of lattice water Sandras. (Konstantinovic et al., 2003; Golcu et al., 2005; Dalia et al., 2018; Hossain et al., 2018). In second step at the range 270-450°C (calculated 75.80-77.87%, experimental 69.00-72.10%), these maximum weight losses are attributable to the loss of coordinated water in agreement with the ligand part ($C_{14}H_9NO_3+H_2O$) (Afsan *et al.*, 2018; Hossain et al., 2018). Above 430-450°C temperature these complexes was decomposed and removed as metal/metal oxide (Cu/CuO, Mn/MnO, Co/CoO) (calculated 22.00-23.50%, experimental 26.80-28.00%) polluted with few carbon atoms. In case of Ni(II) complex lattice water was absent and two steps are as same as other metal complexes. So, thermal analysis of the synthesized complexes confirmed the presence of lattice and coordinated water molecule and supports the proposed structure of the synthesized metal complexes.

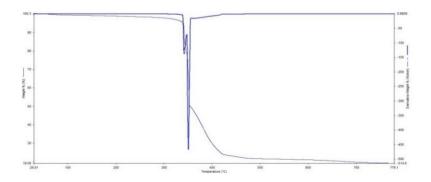


Figure 7. TGA and DTG curve of $[CuC_{14}H_{11}NO_4]$.H₂O Complex

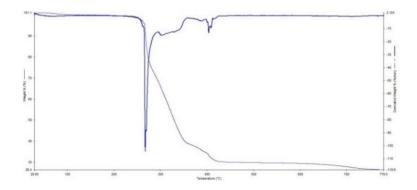


Figure 8. TGA and DTG curve of $[NiC_{14}H_{11}NO_4]$ Complex

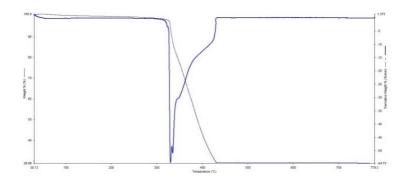


Figure 9. TGA and DTG curve of $[MnC_{14}H_{11}NO_4]$.H₂O Complex

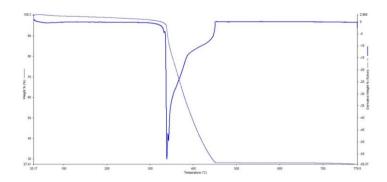


Figure 10. TGA and DTG curve of [CoC₁₄H₁₁NO₄].H₂O Complex

Antibacterial property

The principal objective of performing the antibacterial screening is to determine the susceptibility of the pathogenic microorganism. The free Schiff base ligand and their metal complexes were screened for their antibacterial activity against seven pathogenic bacteria namely *Bacillus cereus, Bacillus subtilis, Escherichia coli, Shigella sonnei, Shigella boydii, Enterobacter* and *Salmonella typhinium*. The compounds were tested at a concentration of 50 μ g/ 0.01 mL in DMSO solution using the paper disc diffusion method (Latif *et al.,* 2019; Govindaraj *et al.,* 2018; Rios *et al.,* 1988). The susceptibility zones measured in diameter (mm) were the clear zones around the discs killing the bacteria. The Schiff base and all the metal complexes individually exhibited varying degrees of inhibitory effects on the growth of tested bacterial species. The results were tabulated in Table 5 and their comparison is shown in Fig. 11. The metal complexes showed greater antibacterial activity as compared with free ligand. This can be explained due to enhanced lipophilic property of the central metal ions as a result of chelation with ligand moieties (Rios *et al.,* 1988).

Tested Bacteria		Diameter of zone inhibition(mm) of tested compounds						
	Ligand, L	[Cu(L)]	[Ni(L)]	[Cd(L)]	[Mn(L)]	[Co(L)]	(30µg/disc)	
Bacillus cereus	6	8	11	12	11	12	20	
Bacillus subtilis	5	10	10	10	13	11	25	
Escherichia coli	5	9	9	11	10	13	25	
Shigella sonnei	5	9	10	12	10	12	22	
Shigella boydii	4	8	11	14	10	14	22	
Enerobacter	4	7	12	12	8	12	24	
Salmonella typhinium	5	9	10	10	11	10	25	

Table 5. Antibacterial activity of the Schiff base and metal complexes

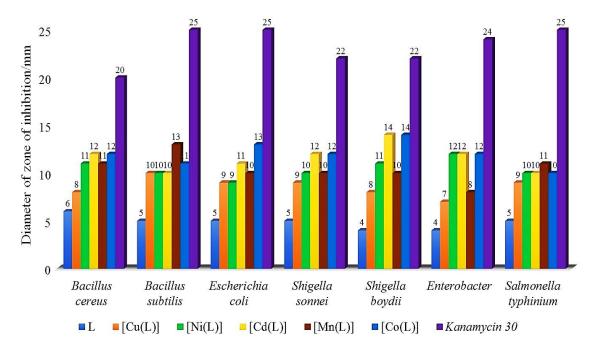


Figure 11. Graphical representation of antibacterial activity of synthesized complexes with Kanamycin 30 standard against Bacillus cereus, Bacillus subtilis, Escherichia coli, Shigella sonnei, Shigella boydii and Enterobacter

Antifungal Screening

The antifungal activity of the complexes were tested by disc diffusion method (Govindaraj *et al.*, 2018; Rios *et al.*, 1988) against the four pathogenic fungi *Candida albicans, Aspergillus niger* and *Aspergillus fumigatus* at a concentration of 200 µg/disc for each. The media used in this respect was potato dextrose -agar (PDA). The activity was determined after 72 hours of incubation at room temperature (25 °C). The maximum zone of inhibition against *Candida albicans, Aspergillus niger and Aspergillus fumigatus species* were found to be 3, 5 and 4 mm; 12, 11 and 13 mm; 11, 12 and 12 mm; 17, 19 and 16 mm; 15, 14 and 11 mm; 12, 14 and 13 mm respectively, for the ligand and its Cu(II), Ni(II), Cd(II), Mn(II) and Co(II) complexes whereas, 22, 23 and 20 mm for standard, nystatin (Table 6) as shown in Fig. 12. The metal complexes showed greater antifungal activity as compared with free ligand. This can be explained on the basis of chelation theory (Mohapatra *et al.*, 2019)

-	Diameter of zone of inhibition (in mm)						
	L	[Cu(L)]	[Ni(L)]	[Cd(L)]	[Mn(L)]	[Co(L)]	Nystatin
μg/disc	200	200	200	200	200	200	50
Candida albicans	3	12	11	17	15	12	22
Aspergillus niger	5	11	12	19	14	14	23
Aspergillus fumigatus	4	13	12	16	11	13	20

Table 6. Antifungal activities of the complexes and standard Nystatin

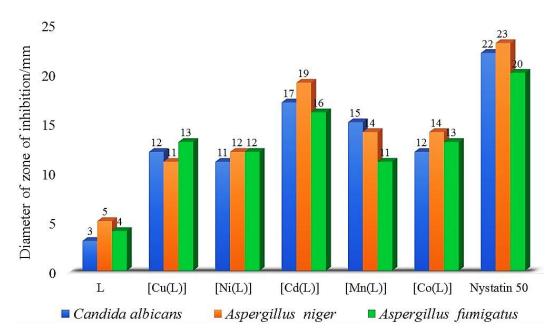


Figure 12. Graphical representation of antifungal activity of synthesized complexes with Nystatin 50 standard against *Candida albicans, Aspergillus niger* and *Aspergillus fumigates*

4. Conclusions

In this paper we have explored the synthesis and coordination chemistry of Cu(II), Ni(II), Cd(II), Mn(II) and Co(II) complexes containing NO donor Schiff base ligand {2-((2-hydroxybenzylidene)amino)benzoic acid} prepared by the condensation of salicylaldehyde and anthranilic acid. The physicochemical analysis indicated the formation of four coordinate metal complexes. FT-IR spectral data indicated that N and O atoms were coordinated to central metal atom. Magnetic moment, UV-visible and thermogravimetric analysis confirmed the proposed tetrahedral structure of Cu(II), Co(II), Cd(II), Mn(II) and square planar structure of Ni(II) metal complexes. TGA analysis indicated that all the complexes are thermally stable up to 200^oC. Antibacterial activity revealed that all the complexes are biologically active against various pathogenic bacterial species and the metal complexes exhibit higher anti-microbial activity than the free ligand.

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References

- Afsan, F., Dalia, S.A., Hossain, S. Sarker, S., & Kudrat-E-Zahan. (2018). Synthesis, Spectral and Thermal Characterization of Selected Metal Complexes Containing Schiff Base Ligands with Antimicrobial Activities. *Asian J. Chem. Sci.*, 4(3), 1-19.
- Alghool, S., Abd El-Halim, H.F., Abd El-sadek, M.S., Yahia, I.S., & Wahab, L.A. (2013). Synthesis, thermal characterization, and antimicrobial activity of lanthanum, cerium, and thorium complexes of amino acid Schiff base ligand. J. Therm. Anal. Calorim., 112(2), 671–681.
- Dalia, M.S.A., Afsan, F., Hossain, M.S., Mannan, M.A., Haque, M.M. & Kudrat-E-Zahan, M. (2018). Spectral and Thermal Characterization of Mn(II), Ni(II) and Zn(II) Complexes Containing Schiff Base Ligands Towards Potential Biological Application. Asian J. Chem. Sci., 4(4), 1-11.
- Elachi, K.A., Hossain, M.S., Bitu, M.N.A., Zahid, A.A.S.M., Mohapatra, R.K., Mannan, M.A., Zakaria, C.M., & Kudrat-E-Zahan, M. (2019). Synthesis, Spectral and Thermal Characterization on Bioactive Complexes of Mg(II), Zn(II), Sn(II), VO(II) and Bi(III) Ions Containing Schiff Base Ligand. J. Chem., Bio., & Phys. Sci., sec. A, 9(4), 201-218.
- Golcu, A., Tumer, M., Demirelli, H., & Wheatley, R.A. (2005). Cd(II) and Cu(II) complexes of polydentate Schiff base ligands: synthesis, characterization, properties and biological activity. *Inorg. Chim. Acta.*, 358(6), 1785-1797.
- Govindaraj, V., Ramanathan, S., & Murgased, S. (2018). Synthesis, Characterization, Antibacterial, Antifungal Screening andCytotoxic Activity of Schiff Base Nickel(II) Complexes with Substituted Benzylidine Aminobenzoic Acid. *Der Chem. Sin.*, 9(3), 736-745.
- Hossain, M.S., Islam, M.A., Zakaria, C.M., Haque, M.M., Mannan, M.A., & Kudrat-E-Zahan, M. (2016). Synthesis, Spectral and Thermal Characterization with Antimicrobial Studies on Mn(II), Fe(II), Co(II) and Sn(II) Complexes of Tridentate N, O Coordinating Novel Schiff Base Ligand. J. Chem. Bio. Phy. Sci., 7(4), 041-052.
- Hossain, M.S., Shaheed, A.S.M.E., Khan, M.N., Mannan, M.A., Haque, M.M., Zakaria, C.M., Mohapartra, R.K., & Kudrat-E-Zahan, M. (2018). Synthesis and Characterization of Cu(II) and Co(II) complexes containing Schiff base ligands towards potential biological application. J. Chem., Bio., & Phy. Sci., 8(4), 654-668.
- Hossain, M.S., Zakaria, C.M., & Kudrat-E-Zahan, M. (2017). Synthesis and Characterization with Antimicrobial Activity studies on some Transition metal complexes of N, O donor novel Schiff base ligand. J. Sci. Res., 9(2), 209-218.
- Islam, R., Uddin, E., Bitu, N.A., Asraf, A., Hossen, F., Haque, M., Mannan, A., & Kudrat-E-Zahan. (2020). Recent Advances in Biological and Catalytic Activities of Schiff base containing Acetylacetone and their Metal Complexes A Short Overview. Asian J. Res. Chem., 13(5), 395-406.
- Jain, A.K., Goyal, R.N., & Agarwal, D.D. (1981). Physico-chemical studies on some metal chelates of 5,5 dimethylcyclohexane-2-(2-hydroxyphenyl)hydrazono 1,3 dione (DCPHD). *J. Inorg. Nucl. Chem.*, 43(9), 2005-2009.
- Jezowska-Trzebiatowska, B., Lisowski, J., Vogt, A., & Chmielewski, P. (1988). Synthesis and characterization of Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes with N-salicydene-o-hydroxymethyleneaniline. *Polyhedron*, *7*(5), 337-343.

- Konstantinovic, S.S., Radovanovic, B.C., Cakic, Z., & Vasić, V.M. (2003). Synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 3salicylidenehydrazono-2-indolinone. J. Serb. Chem. Soc., 68(8–9) 641-647.
- Latif, M.A., Tofaz, T., Chaki, B.M., Islam, H.M.T., Hossain, M.S., & Kudrat-E-Zahan, M. (2019) Synthesis, Characterization, and Biological Activity of the Schiff Base and Its Ni(II), Cu(II), and Zn(II) Complexes Derived from 4-(Dimethylamino)benzaldehyde and S-Benzyldithiocarbazate1. *Russian J. Gen. Chem.*, 89(6), 1197-1201.
- Lindoy, L.F., Moody, W.E., & Taylor, D. (1977). Mass spectral and nuclear magnetic resonance (proton and carbon-13) study of metal complexes of quadridentate ligands derived from 1,2-diaminoethane and substituted .beta.-diketones; x-ray structure of N,N'- ethylenebis(5,5-dimethyl-4-oxohexan-2-iminato)nickel(II). *Inorg. Chem.*, *16*(8), 1962-1968.
- Liu, X. & Hamon, J.R. (2019). Recent developments in penta-, hexa- and heptadentate Schiff base ligands and their metal complexes. *Coord. Chem. Rev.*, *389*, 94-118.
- Mohapatra, R.K., Das, P.K., Pradhan, M.K., El-Ajaily, M., Das, D., Salem, H.F., Mahanta, U., Badhei, G., Parhi, P.K., Maihub, A.A., & Kudrat-E-Zahan, M. (2019). Recent Advances in Urea- and Thiourea-Based Metal Complexes: Biological, Sensor, Optical, and Corroson Inhibition Studies. *Comm. on Inorg. Chem.*, 39(3), 127-187.
- Mohapatra, R.K., Sarangi, A.K., Azam, M., El-ajaily, M.M., & Kudrat-E-Zahan, M., Patjoshi, S.B., Dash, D.C. (2019). Synthesis, structural investigations, DFT, molecular docking and antifungal studies of transition metal complexes with benzothiazole based Schiff base ligands. J. Mol. Struc., 1179, 65-75.
- Raman, N., Kulandaisamy, A., Shunmugasundaram, A., & Jeyasubramanian, K. (2001). Synthesis, spectral, redox and antimicrobial activities of Schiff base complexes derived from 1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one and acetoacetanilide. *Trans. Metal Chem.*, 26(1), 131-135.
- Rios, J.L., Recio, M.C., & Villar, A. (1988). Screening methods for natural products with antimicrobial activity: A review of the literature. *J. Entho. Pharmacol.*, 23(2-3), 127-149.
- Seco, J.M., Quirós, M., & Garmendia, M.J.G. (2000). Synthesis, X-ray crystal structure and spectroscopic, magnetic and EPR studies of copper(II) dimers with methoxy-di-(2pyridyl)methoxide as bridging ligand. *Polyhedron*, 19(8), 1005-1013.
- Singh, H.L., & Singh, J.B. (2014). Synthesis, Spectroscopic, Molecular Structure, and Antibacterial Studies of Dibutyltin(IV) Schiff Base Complexes Derived from Phenylalanine, Isoleucine, and Glycine. *Bioinorg. Chem. and Appl.*, Article ID 716578, 1-12.
- Soliman, E.M., El-roudi, A.M., Hassaan, A.M., & Refaiy, S.A. (1989). Lanthanum(III), Cerium(III), Thorium(IV) and Uranium(VI) Complexes of Some Quinoline Derivatives. Synth. React. Inorg. Met. Org. Chem., 19(9), 957-967.
- Zabin, S.A., Jammali, M., & Alzahrani, A.A. (2018). The Bivalent Cu, Ni and Zn Complexes of Unsymmetrical ONO Tridentate Schiff Base Ligands Derived from 2-Aminobenzoic Acid: Antimicrobial and Molluscicidal Activity. J Org. & Inorg. Chem., 4(2), 1-6.
- Zhang, J., Xu, L., & Wong, W.Y. (2018). Energy materials based on metal Schiff base complexes. *Coord. Chem. Rev.*, 355, 180-198.